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(54) SUBSTRATE FOR PATTERNING THIN FILM AND SURFACE TREATMENT THEREOF

(57) Display devices such as EL elements or LED elements, or color filters, are provided, wherewith, when forming thin films such as organic semiconductor films or colored resins, there is remarkably little variation in film thickness from pixel to pixel. When fabricating thin film elements having banks of a prescribed height and a thin film layer formed by an ink jet method in areas to be coated that are partitioned by those banks, if the width of the banks is made a (鍛), the height thereof is made c (鍛), the width of the areas to be coated is made b (鍛), and the diameter of the liquid droplets of the liquid material forming the thin film layer is made d (鍛), the banks are formed on the substrate so as to satisfy the conditions that $a > d/4$, $d/2 < b < 5d$, $c > t_0$ (where t_0 (鍛) is the film thickness of the thin film layer), and $c > 1/2 \times d/b$. Furthermore, banks are formed of an organic material on a bank formation surface configured of an inorganic material, plasma treatment is performed under conditions that the induction gas is fluorine-based and that fluorine is present excessively, and the areas enclosed by the banks subjected to surface

treatment are filled with the liquid thin film material to form the thin film layer or layers. Also, immediately after performing an oxygen gas plasma treatment on the substrate having the banks formed of

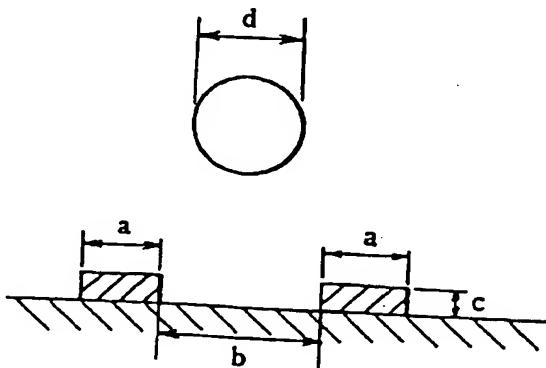


FIG.1

Description**TECHNICAL FIELD**

5 [0001] This invention relates to thin film formation technology suitable for manufacturing color filters or display elements such as LEDs (light emitting diodes) or EL (electro-luminescence) devices which use organic semiconductor films.

10 [0002] More particularly, the present invention relates to substrates, a thin film formation method, and thin film elements used in forming patterns on substrates when thin films having different properties are formed on the same substrate. The present invention also relates to a method of forming thin films on which fine patterning is required, wherewith it is both easy to form thin film layers using an ink jet process and possible to form flat thin film layers. The present invention further relates to a surface modification method for performing superfine patterning wherewith a liquid thin film material is deployed in areas enclosed in banks formed on a substrate, using an ink jet method or spin coating, etc., as well as to a method that employs this surface modification method in forming thin films and to both a display element comprising such a thin film and a manufacturing method therefor.

BACKGROUND ART

15 [0003] In recent years, technology has been under development for obtaining functional devices by forming prescribed patterns by applying thin films having differing properties on the same substrate. One promising method therefor uses an ink jet process in forming patterns with different thin film patterns on the same substrate. When an ink jet process is used, however, a problem arises at the process surface in that the different thin film materials become mixed on the substrate. In more specific terms, the technology used employs an ink jet process in applying an organic semiconductor material in producing EL devices or other display elements, or a colored resin or other thin film material in producing color filters, but, when the ink jet process is used to deploy a liquid material when forming a thin film pattern, the liquid material that is discharged flows over into adjacent pixels. This presents a problem.

20 [0004] What is commonly done to overcome problems such as this is to provide protruding partitioning members (called "banks" or "risers") to partition off different thin film areas, and then to fill the areas enclosed by these partitioning members with the liquid materials constituting the different thin films. In the display element example noted above, a method is adopted wherein partitioning members are provided to partition off the various pigment areas, and filling the areas enclosed by the partitioning areas with the materials that configure the pixels.

25 [0005] In recent functional devices, and particularly in display elements, thinness is generally demanded, and, despite the fact that this places limitations on the height of the partitioning members, the volume of liquid material deployed in the areas enclosed by the partitioning members is far greater than the volume remaining after film fabrication.

30 [0006] For this reason, problems arise in terms of poor balance between the size of the liquid droplets discharged into the areas enclosed by the partitioning members and the surface areas both of the partitioning member surfaces and of the areas enclosed therein. This problem will now be described further.

35 [0007] In cases where the partitioning members exhibit liquid affinity or wettability relative to the liquid material that is the thin film material to be deployed, the desired film thickness cannot be obtained in the final thin film even when partitioning members are present since [the liquid material] is pulled by the partitioning members. If the volume of liquid material is made greater, moreover, the liquid material readily flows out into the adjacent areas.

40 [0008] Nevertheless, the surfaces of the areas enclosed by the partitioning members need to exhibit strong liquid affinity and wettability relative to the liquid material so that the liquid material will uniformly wet and spread over those surfaces. If that is not the case, the liquid material will not wet and spread over the areas enclosed by the partitioning members, and, with display elements such as EL devices, in particular, color loss and color irregularity will develop in the pixels.

45 [0009] To deal with problems such as these, technology is proposed in Japanese Patent Laid-Open No.09-203803 and Japanese Patent Laid-Open No.09-230129, as published, for example, wherein surface treatments are employed to make the upper portions of the partitioning members liquid-repellant and to make the other portions exhibit liquid affinity.

50 [0010] In all of these examples of the prior art, a layer composed of a liquid-repellant material (a layer made of a fluorine compound) is formed on the upper surface of the partitioning members. In Japanese Patent Laid-Open No.09-203803, as published, technology is cited wherein a layer exhibiting non-affinity is coated onto the upper portions of the partitioning members, and the surfaces of the areas enclosed by the partitioning members are treated with a hydrophilic base-surface-active agent. In Japanese Patent Laid-Open No.09-230129, as published, technology is cited for giving the recessed portions enclosed by the partitioning members affinity by additionally exposing them to UV radiation. The theoretical background for this is set forth in "International Display Research Conference 1997," pp 238-241.

55 [0011] However, even when water repellency in the upper surfaces of the partitioning members and liquid affinity in the areas enclosed by the partitioning members are to some degree realized, in cases where the liquid material is applied using an ink jet process, for example, if the size of the liquid droplets discharged is extremely large or small relative to the surface area of the surfaces of the partitioning members noted above or of the areas enclosed thereby, or if the balance therebetween is otherwise very poor, it is known that the liquid material is not

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accurately deployed in the areas coated, so that high-precision patterning becomes impossible. When, for example, the size of the liquid droplets noted above is larger than the areas enclosed by the partitioning members to too great an extent, the liquid droplets cross over the partitioning members, and, when the upper surfaces of the partitioning members are narrow, the liquid droplets spill over into areas adjacent to the areas being coated.

[0012] In cases such as this, when there is an unsuitable relationship between liquid droplet size and the surface area of the areas enclosed by the partitioning members, what happens is that, due to the problems noted earlier, liquid thin film materials become mixed together in the areas enclosed by the partitioning members, and film thickness variation develops in each thin film that is formed.

[0013] Problems also arise which relate to the affinity of the partitioning members toward the liquid thin film material when that thin film material is deployed in the areas demarcated by the partitioning members.

[0014] The behavior of the liquid thin film material deployed differs according as to what sort of wettability (affinity) toward the liquid thin film material is exhibited by the partitioning members or the areas enclosed by the partitioning members. As noted earlier, when the surfaces of the partitioning members exhibit affinity (hydrophilic property) toward the liquid thin film material, and the volume of the material deployed exceeds the height of the partitioning members, that liquid thin film material will readily flow over into neighboring areas enclosed by partitioning members even when such partitioning members exist. Conversely, when the surfaces of the partitioning members exhibit a proper degree of non-affinity (water repellency) toward the liquid thin film material, that liquid thin film material will not flow over into the neighboring areas enclosed by partitioning members even when the volume of material deployed exceeds the height of the partitioning members, due to the surface tension of the material.

[0015] There are also more specific substrate surface modification methods, such as, for example, those described in the previously cited Japanese Patent Laid-Open No.09-203803 and Japanese Patent Laid-Open No.09-230129, as published, and also in Japanese Patent Laid-Open No.09-230127, as published. That is, specifically, technology involving a method for subjecting bank surfaces to an ink-repellency treatment with a fluorine compound (Japanese Patent Laid-Open No.09-203803, as published), an etching treatment method (Japanese Patent Laid-Open No.09-230127, as published), and ink-affinity treatment using energy irradiation (Japanese Patent Laid-Open No.09-230129, as disclosed).

[0016] Nevertheless, when member surfaces are made ink-repellent using a fluorine compound or members are formed using a fluorine compound material, in particular, the bonding strength between the fluorine-based material and the underlying layer or underlying substrate forming the members becomes poor, which presents problems in terms of applications to bank-forming technology. Even if the members, and particularly the banks themselves, are formed with an ink-repellent fluorine compound material or the like, residue develops in the bank areas after patterning by photolithography, whereupon there is a danger of the ink affinity of the bank surfaces being impaired.

[0017] In the prior art described in the foregoing, moreover, the application, drying, and removal of materials exhibiting non-affinity are necessary just to impart non-affinity to the upper portions of the partitioning members, whereupon the number of process steps inevitably becomes large. Also, when UV irradiation is performed, there is a tendency for affinity with many materials to develop. There has been a tendency for a slight affinity to develop due to UV irradiation, even when the material is one exhibiting non-affinity, thereby negating the effectiveness of the non-affinity treatment. In Japanese Patent Laid-Open No. 09-230129, as published, in particular, there is a provision to the effect that the degree of affinity be controlled by subjecting both the front and back sides to UV radiation, but, in terms of controlling the affinity between non-affinity and affinity, it is not specified how the various angles of contact relative to the liquid thin film material should be established.

[0018] When the liquid repellency of the partitioning members is strong, moreover, the liquid of the thin film material is repelled by the side walls of the partitioning members, wherefore the thickness after film formation becomes thick in the center portions of the areas enclosed by the partitioning members and thin about the peripheries thereof. This results in color irregularities in the pixels in the display elements. In EL devices, in particular, shorts readily develop, leading to reduced reliability.

[0019] When the surfaces of the partitioning members are subjected to a liquid-repellency treatment and affinity (liquid-affinity) is imparted to the side surfaces thereof, a thin film material is provided wherewith the thickness after film formation does not become thin about the peripheries of the areas enclosed by the partitioning members. Nevertheless, because most of the liquid of the thin film material is pulled to the side surfaces of the partitioning members, not only does the film thickness become greater in the lower skirt portion of the thin film, that is, in the portions in contact with the substrate, but neither is it difficult to control the film thickness.

[0020] There are known methods of modifying the surface energy (wettability) of an organic substance which involve performing a plasma process. One example of such a surface modification method is that described in Japanese Patent Laid-Open No. 63-308920/1988, as published. In the surface modification method set forth in this publication, the organic substance surface is treated with a mixed gas plasma containing a fluorine-based gas and gaseous oxygen, and the surface energy of the organic substance is controlled by varying the mixture ratios between the mixture gasses.

[0021] Methods involving UV irradiation or oxygen plasma treatment are also well known as procedures for making the surfaces of organic substances such as glass or indium tin oxide (ITO) hydrophilic.

[0022] No technology has been reported, however, for simply and rigorously controlling the wettability of each material in the substrate by plasma treatment or UV irradiation in cases where a pattern of layers constituted by organic or inorganic substances is formed on the same substrate. With methods wherein ink repellency is imparted by mixture-gas plasma treatment to an organic substance surface or the surface of a member formed of an organic substance, problems arise, such as being unable to impart ink repellency efficiently, or that the ink repellency of the surface is transient, or having to use a heat treatment, so that the ink repellency deteriorates with the passage

of time.

[0023] In cases where an ink-affinity treatment is performed using energy irradiation, there is a danger of impairing the ink repellency of the bank surfaces, and it is very difficult to simultaneously achieve both bank surface ink repellency and bank surface ink affinity.

[0024] In methods for forming thin films in prescribed patterns where different thin film materials are provided, and particularly in methods for forming thin films wherein liquid thin film materials are deployed in areas enclosed by partitioning members (banks) formed on a substrate, the proper control of wettability (ink repellency and ink affinity) in the banks and depressions is critical. If the banks do not exhibit ink repellency, not only will ink residue develop on the banks, but, in cases where different liquid thin film materials are deployed in adjacent depressions divided by a bank, those different liquid thin film materials will overflow the bank and be mixed together. When this happens, it is not possible to form thin films having the desired characteristics.

[0025] Examples of the formation of thin films using different liquid thin film materials in adjacent depressions divided by banks include color organic EL devices and color filters used in liquid crystal display elements, etc. When these devices are manufactured, however, the banks must exhibit ink repellency and the areas enclosed by the banks, that is, the surfaces of the ITO or glass substrate, must exhibit ink affinity. If the depressions do not exhibit ink affinity, the wetting and spreading within the pixels will be poor, causing color loss and film thickness irregularity.

[0026] With the methods described in the foregoing, moreover, in addition to the ink-repellency treatment, an ink-affinity treatment process is also necessary in the pixel areas, that is, in the depressions. Thus these methods involve difficulties in that controlling the ink supplied is difficult and in that the number of process steps becomes large.

DISCLOSURE OF THE INVENTION

[0027] It is in the face of these circumstances that the present invention was arrived at. The primary objects of the present invention are, when forming film patterns using thin films of different properties on the same substrate, to prevent liquid thin film materials from flowing over the banks, to be able to form thin film layers that are flat and of uniform thickness with no color irregularities, without fail, with high precision, relatively simply, and with good yield, and to make possible very fine and highly detailed patterning.

[0028] A first object of the present invention is to provide thin film elements such as organic EL devices and color filters that—when thin films of an organic semiconductor material or colored resin, etc., are formed by a discharge method such as ink jetting or bubble jetting—are patterned to high precision without the occurrence of mixing in any of the thin film areas, and with remarkably little variation in film thickness. Another object of the present invention incidental to the first object is to provide the thin film patterning substrates to be used when manufacturing these thin film elements, display elements comprising such thin film elements, and thin film formation methods for obtaining these thin film elements.

[0029] A second object of the present invention is to provide substrate thin film elements and thin film formation methods wherewith even finer patterning is possible when forming interconnections or other electrically conducting thin films for semiconductor devices, electronic devices, and the like, by a spin-coating or dip method, together with thin film elements formed by such methods, display elements comprising these thin film elements, and electronic equipment comprising these display elements, respectively.

[0030] A third object of the present invention is to provide a method for modifying the surface of a substrate whereon are formed banks for the purpose of conveniently and suitably controlling wettability, together with methods for forming thin films using that surface modification method, display elements and display devices comprising these thin films, and manufacturing methods therefor.

[0031] A fourth object of the present invention is to provide a thin film formation method wherewith, by managing a plasma process under certain conditions, the affinity between banks and bank formation surfaces can be definitely controlled while the banks themselves maintain high bonding strength with the bank formation surfaces, without requiring numerous process steps for affinity control. Thus the liquid thin film material is prevented from flowing over the banks, yield is improved, and manufacturing costs are reduced.

[0032] A fifth object of the present invention is to provide display devices wherewith the liquid thin film material is prevented from flowing over the banks by definitely establishing the affinity between the banks and the bank formation surfaces by managing a plasma process under certain conditions, which display devices have thin film layers of uniform thickness. Thus image display can be effected wherein no irregularities in brightness or color appear, and wherewith reliability is enhanced.

[0033] As a result of conducting assiduous research for the purpose of achieving the first object noted above, the inventors discovered that the first object of the present invention can be achieved, in forming thin films using the discharge methods described earlier, by not only adjusting the liquid repellency of the partitioning member surfaces noted above for a liquid material and the liquid affinity of the areas enclosed by the partitioning members, but also optimizing the relationship between the size of the liquid droplets of the liquid material discharged and the surface areas of the partitioning members and the areas enclosed by those partitioning members.

[0034] [The inventors] also discovered that, when forming thin films by spin-coating or dipping, in addition to controlling the liquid-material wettability of the partitioning members and the areas enclosed by the partitioning members, by adjusting the surface tension of this liquid material to a certain value, the second object of the present invention, stated above, can be achieved. The present invention was perfected on the basis of such discoveries as these.

[0035] Specifically, in order to achieve the first object noted earlier, the present invention is either a thin

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film patterning substrate comprising a thin film layer pattern formed by an ink jet method on banks of a prescribed height and in areas to be coated which are demarcated by those banks, or a display element formed on that patterning substrate, characterized by the fact that, when the width of the banks is made a (鰄), the height thereof is made c (鰄), the width of the areas to be coated is made b (鰄), and the diameter of the liquid droplets of the liquid material or materials forming the thin film layer or layers is made d (鰄), the banks exhibit the following characteristics.

5 (1) The banks are formed on the substrate so as to satisfy the relationship $d/2 < b < 5d$. By satisfying this characteristic range, the liquid material will not ride up on the banks, and color mixing inside the pixels is prevented. In addition, this characteristic is augmented by at least one of the following characteristics.

10 (2) $a > d/4$: When b is small, if $a > d/4$, then the liquid material may ride up on the banks, but mixture of thin film materials inside the areas to be coated is prevented.

15 (3) $c > t_0$ (where t_0 is the film thickness of the thin film layer (in 鰄))

20 (4) $c > d/2b$

15 [0036] In cases where the areas to be coated are stripes or square in shape, the parameters a and c noted above will be constant, but when the pixels are circular, parameter a becomes the shortest distance between pixels, and parameter c becomes the diameter.

20 [0037] The present invention for achieving the second object noted earlier is a thin film element formed so that it has banks of a specific height formed on the substrate, areas to be coated demarcated by those banks, and thin film layers formed by a dipping or spin-coating method in those areas, characterized by the fact that the thin film layers are formed using a substrate subjected to prescribed surface treatment ([for] wettability control), and using liquid material having a surface tension of 30 dyne/cm or less.

25 [0038] By keeping the surface tension of the liquid synthetic resin within this range, it is possible to form patterned thin films of a width of a few microns or less, using a spin-coating or dip method.

30 [0039] The present invention provides thin film formation methods for obtaining these thin film elements, display devices comprising these thin film elements as the display elements, and, furthermore, electronic equipment comprising these display devices.

35 [0040] The invention concept common to the inventions described below and devised by the inventors for achieving the third and following objects noted earlier is a surface modification method for filling areas enclosed by banks on a substrate with a thin film forming material. [The third and following objects are further achieved by] surface modification technology having processes for uniformly subjecting the entire surface of the substrate on which the banks are formed to a series of surface modification treatments, and, by means of that series of treatments, to raise the non-affinity of the bank portion surfaces to the thin film formation material relative to that of the surface of the portions between banks, or by thin film formation technology wherein that surface modification technology is employed, or a thin film patterning substrate wherein that is used, or a display element such as an EL device wherein that is used, or a display apparatus wherein that element is used.

40 [0041] Whereas with the examples of the prior art described earlier, patterning is done after subjecting the entire surface of a photoresist prior to patterning to a water repellency treatment to yield a surface-treated bank pattern, or a surface treatment is performed wherewith masking is done after forming the banks, as based on the present invention, a series of treatments is performed indiscriminately on almost the entire surface of a substrate on which banks have been preformed, whereupon the surface treatments sought can be performed all at once, so that no process of a different type than the surface treatment is involved during the course of plasma treatment or other surface treatment. What is here called a series of surface modification treatments refers to a process, described below, for, most suitably, applying plasma treatments, described below, all at one time to a substrate wherein banks made of an organic material are formed on bank forming surfaces configured by an inorganic material.

45 [0042] Thereupon, the invention for achieving the third object noted earlier is a surface modification method for filling areas enclosed by banks on a substrate with a thin film forming material, comprising: a bank formation process for forming banks with an inorganic material on bank formation surfaces configured by an inorganic material; and a surface treatment process for subjecting the banks and the bank formation surfaces to surface treatment, in cases where prescribed surface treatment has been performed, under certain conditions such that the degree of non-affinity exhibited by the banks for the liquid thin film material becomes higher than that of the bank formation surfaces.

50 [0043] Another aspect of this invention is a thin film formation method for filling the areas enclosed by the banks with a thin film forming material and forming a thin film layer or layers, comprising: a bank formation process for forming banks with an inorganic material on bank formation surfaces configured by an inorganic material; a surface treatment process for subjecting the banks and the bank formation surfaces to surface treatment, in cases where prescribed surface treatment has been performed, under certain conditions such that the degree of non-affinity exhibited by the banks for the liquid thin film material becomes higher than that of the bank formation surfaces; and a thin film layer formation process for filling the areas enclosed by the banks subjected to surface treatment with the liquid thin film material and forming a thin film layer or layers.

55 [0044] What is meant by bank here, as described earlier, is a partitioning member provided for partitioning pixels in a display device wherein organic semiconductor thin film elements are used, for example, or for partitioning pixel areas in a color filter, etc. By bank formation surface is meant a surface on which banks are made,

which may be a drive substrate for a display device, etc., or a transparent substrate or the like for a color filter, etc.

[0045] For the surface treatment, a reduced-pressure plasma treatment or atmospheric-pressure plasma treatment is performed wherein plasma irradiation is conducted in a reduced-pressure atmosphere or atmospheric-pressure atmosphere, respectively, using an induction gas containing fluorine or a fluorine compound, for example. The certain conditions refer, for example, to the performance of the plasma treatment in a gas containing a fluorine-based compound and oxygen. Under these conditions, unreacted groups are generated by plasma discharge on the surface of the inorganic material, those unreacted groups are oxidized by the oxygen, and polar groups such as carbonyl or hydroxide groups are generated. Polar groups exhibit affinity toward fluids which contain polar molecules such as water, but exhibit non-affinity toward fluids which contain nonpolar molecules. On the organic material surface also, in parallel with the reaction described above, a phenomenon occurs whereby fluorine-based compound molecules invade the organic material surface. In particular, when there is more of the fluorine-based compound than there is of oxygen, and the quantity of the fluorine-based compound is set at 60% or more relative to the total quantity of the fluorine-based compound and the oxygen, the effect of the fluorine-based compound mixing becomes dominant over the oxidation reaction with the oxygen in a gas atmosphere wherein the quantity of the fluorine-based compound has become excessive, wherefore the surface is rendered nonpolar due to that mixing phenomenon which is stronger than the influence of the oxidation reaction. Accordingly, when the organic material is plasma-treated under conditions of excessive fluorine-based compound, non-affinity toward fluids containing polar molecules will be exhibited, while affinity will be exhibited toward fluids containing nonpolar molecules.

[0046] The gases used for the gas containing fluorine or a fluorine-based compound include, for example, CF_4 , SF_6 , and CHF_3 , etc. When the surface treatment is performed under these conditions, the surface affinity thereof is adjusted so that the angle of contact with the fluid between the organic material and inorganic material becomes greatly divergent. The surface treatment conditions are set by the surface treatment described above so that the angle of contact with the bank formation surface of the liquid thin film material becomes 20 degrees or less. The surface treatment conditions are also set so that the angle of contact with the bank formation surface of the liquid thin film material becomes 50 degrees or greater. When the banks are formed in two layers, the affinity of the lower bank layer for the liquid thin film material is set, by a surface treatment, so that it is equal to or lower than that of the pixel electrodes but equal to or greater than that of the upper bank layer. The surface treatment conditions are set, for example, so that the surface of the upper bank layer subtends an angle of contact with the liquid thin film material of 50 degrees or less. And the surface treatment conditions are set so that the angle of contact subtended by the lower bank layer with the liquid thin film material is within a range of 20 to 40 degrees.

[0047] Whether affinity or non-affinity is exhibited here is determined by the properties of the liquid thin film material that is deployed. If the liquid thin film material is hydrophilic, for example, the surfaces having polar groups will exhibit affinity, while the surfaces having nonpolar groups will exhibit non-affinity. Conversely, if the liquid thin film material exhibits oil-affinity, the surfaces having polar groups will exhibit non-affinity, and the surfaces having nonpolar groups will exhibit affinity. The thin film materials used will vary widely according to the manufacturing objective.

[0048] It is preferable that the bank formation process form two layers of banks, namely an upper layer and a lower layer. In one specific example, this bank formation process comprises a lower film layer formation process for forming a lower film layer on the bank formation surfaces, an upper layer formation process for forming an upper layer in conformity with the bank formation areas on the lower film layer, and a removal process that uses the upper layer as a mask and removes, by etching, the lower film layer in the areas where that upper layer is not provided.

[0049] In another specific example, the bank formation process comprises a lower film layer formation process for forming a lower film layer on the bank formation surfaces, a process for exposing and developing that lower film layer in conformity with the lower bank layer formation areas, an upper film layer formation process for forming an upper film layer covering the lower layer, and a process for exposing and developing that upper film layer in conformity with the upper bank layer formation areas.

[0050] In one example application, pixel electrodes are provided in areas enclosed by banks, and the liquid thin film material is an organic semiconductor material for forming thin film light emitting elements. This is an organic semiconductor display device. The pixel electrodes here may be, for example, ITO electrode films. In specific terms, it is desirable that the banks be made of an insulating organic material such as a polyimide. In cases where a lower bank layer is provided, moreover, silicon oxide film, silicon nitride film, or amorphous silicon is used.

[0051] The present invention for achieving the fourth object noted earlier is a surface modification method for filling areas enclosed by banks formed on a substrate with a liquid thin film material. This invention provides a surface modification method which comprises a first process for performing an oxygen plasma treatment on the substrate whereon the banks are formed, and a second process for performing, consecutively, a fluorine-based gas plasma treatment.

[0052] By using this method, the surface of the glass, ITO, or other inorganic substrate can be made to exhibit liquid-affinity (affinity) for the liquid thin film material noted above.

[0053] The oxygen plasma treatment performed in the first process noted above not only ashess the residue in cases where banks are formed of organic substances on the substrate, but also activates the surface of the organic substance. This is effective in performing liquid-repellency treatment more efficiently in the fluorine-based gas plasma treatment performed immediately thereafter.

[0054] In the second process noted above, fluorine-based gas plasma treatment is performed whereby the surface of the organic substance is fluoridized (Teflon-treated), making it possible to impart semi-permanent liquid repellency to the organic substance. With this fluorine-based gas plasma treatment, the liquid affinity exhibited on the substrate is not impaired, and surfaces exhibiting liquid affinity and liquid repellency can be selectively

formed on the substrate by a simple method.

[0055] Furthermore, at least one of the plasma treatments of the first and second processes described in the foregoing may employ an atmospheric-pressure plasma in a treatment performed under atmospheric pressure. Alternatively, at least one of the plasma treatments of the first and second processes described in the foregoing may employ a reduced-pressure plasma in a process performed under reduced pressure.

5 [0056] If the degree of contamination on the substrate is low, moreover, it is permissible to perform only the fluorine-based plasma treatment. In particular, with a reduced-pressure plasma, the substrate surface can be cleaned, and the organic substance forming the banks can be Teflon-treated.

[0057] The substrate mentioned in the foregoing can be configured from an inorganic substance. A substrate surface made of such an inorganic substance can also be made to exhibit liquid affinity.

10 [0058] It is possible to form at least the upper surfaces of the banks formed on the substrate noted above from an organic substance. Alternatively, both the upper surfaces and side surfaces of the banks formed on the substrate can be formed of an organic substance. It is further permissible to form the banks formed on the substrate in two layers whereof the lower layer is formed of an inorganic substance and the upper layer is formed of an organic substance. Alternatively, the banks formed on the substrate can be formed in two layers, whereof the lower layer is formed of an inorganic substance and the upper layer is formed of an organic substance, such that at least the side surfaces of the inorganic substance are not covered by the organic substance.

15 [0059] The surfaces of the organic substance forming the banks may also be made to exhibit liquid repellency (non-affinity). Or the surfaces of the organic substance forming the banks may be Teflon-treated. Alternatively, the surface of the organic substance forming the banks can be made to exhibit liquid repellency and the surface of the substrate formed of one of the inorganic materials noted earlier can be made to exhibit liquid affinity.

20 [0060] Because it is not necessary to use a material that already exhibits liquid affinity for the organic material forming the banks, the range of materials that may be selected is broadened.

[0061] Also, surface energy (liquid affinity, liquid repellency) can easily be controlled by such conditions as process time, gas type, gas flow volume, plasma intensity, and the distance from the plasma electrode to the substrate, etc.

25 [0062] The angle of contact subtended by the liquid thin film material noted in the foregoing with the surface of the substrate noted in the foregoing can be made 30 degrees or less, and the angle of contact subtended with the bank surfaces noted above can be made 50 degrees or more.

[0063] When the angle of contact subtended by the liquid thin film material with the substrate surface exceeds 30 degrees, the liquid thin film material will not wet and spread over the entire surface of the substrate enclosed by the banks or it will not uniformly wet and spread, so that film thickness irregularities will develop. When, on the other hand, the angle of contact subtended by the liquid thin film material with the bank surfaces is less than 50 degrees, the liquid thin film material adheres to the upper portions of the banks, or is pulled to the bank sides and exceeds the banks, thus flowing into the adjacent substrates. In other words, it becomes impossible to effect patterns of the liquid thin film material at the desired locations.

30 [0064] Furthermore, by forming the banks in two layers, using an inorganic material for the lower layer, and effecting control so that the angle of contact is from 20 to 50 degrees, the problem of the film not adhering to or becoming thin at the skirts of the banks can be resolved.

35 [0065] Accordingly, it becomes possible to employ an ink jet method or spin-coating method to effect liquid thin film material patterning with high precision in areas enclosed by banks using the surface modification method described in the foregoing. If a substrate subjected to surface modification as described above and a thin film formation method based on the ink jet method is employed, it becomes possible to manufacture very fine color filters and full color EL devices simply and at low cost.

40 [0066] The present invention for achieving the fifth object, furthermore, is a method for forming thin films wherewith areas enclosed by banks formed on a substrate are filled with a liquid thin film material. This invention provides a thin film formation method which comprises a process for filling areas enclosed by banks on a substrate subjected to the surface modification described in the foregoing with the liquid thin film material noted earlier, by an ink jet method, immediately after the surface modification.

45 [0067] The present invention, furthermore, for achieving the fifth objective, is a method for forming thin films by filling areas enclosed by banks formed on a substrate with a liquid thin film material, providing a thin film formation method that comprises a process for filling the areas enclosed by the banks on the substrate subjected to the surface modification described in the foregoing with the liquid thin film material noted above, by a spin-coating or dipping method, immediately after that surface modification.

[0068] The present invention, furthermore, for achieving the fifth object, provides display devices which comprise thin films formed by the thin film formation method described above. These display devices can be constituted of color filters or organic EL elements or the like.

50 [0069] The present invention, moreover, in order to achieve the fifth object, provides methods for manufacturing display devices wherein thin films are formed by the thin film formation methods described in the foregoing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0070]

55 Fig. 1 is a simplified explanatory diagram of the relationship between liquid droplets and a display device of the present invention;

gas plasma conditions being an oxygen gas flow volume of 80 ccm, a helium gas flow volume of 10 liters/min, and a transporting speed of 10 mm/s, and the CF₄ plasma conditions being a CF₄ gas flow volume of 100 ccm, a helium gas flow volume of 10 liters/min, and a transporting speed of 5 mm/s. It is very effective to use atmospheric-pressure plasma because the time required to create a vacuum in the process chamber can be saved and the same surface modification can be effected more simply.

[0200] When a fluorine-based gas plasma treatment is performed, although CF₄ was used in the case described above, this does not pose a limitation, and other fluorine-based gasses such as NF₃ and SF₆, for example, can be used.

[0201] It is possible to control the wettability (surface energy) not only by the process time, but also by such parameters as the gas flow volume, power, and electrode-substrate distance, etc.

[0202] Thus it is possible with the same consecutive oxygen-CF₄ plasma processing to perform surface modification so as to effect liquid affinity in an inorganic substance surface and liquid repellency in an organic substance surface.

(9) Ninth Embodiment

[0203] A thin film formation method and a manufacturing method for organic EL elements comprising organic semiconductor thin films relating to a ninth embodiment of the present invention are now described, making reference to the drawings.

[0204] Fig. 23A - 23E are process cross-sections representing a method of manufacturing organic EL elements.

[0205] In the process diagrammed in Fig. 23A, banks 302 made of a polyimide are formed by photolithography on an ITO substrate 301. The pattern may be a striped pattern or a pattern wherein circular shapes are removed. The material forming the banks is not limited to a polyimide, and any organic material capable of patterning by photolithography can be used.

[0206] In the process diagrammed in Fig. 23B, an oxygen plasma treatment is performed for 1 minute with an oxygen gas flow volume of 500 SCCM, power of 1.0 W/cm², and pressure of 1 torr as conditions. Atmospheric-pressure plasma treatment can also be performed with a power of 300 W, electrode-substrate distance of 1 mm, oxygen gas flow volume of 80 ccm, helium gas flow volume of 100 liters/min, and transporting speed of 10 mm/s. In the oxygen plasma treatment a hydrophilic ITO surface 3 and a polyimide layer 304 that is activated (made hydrophilic) are formed. The oxygen plasma treatment exhibits effectiveness in ashing polyimide residue on the ITO.

[0207] Following thereupon, in the process diagrammed in Fig. 23C, CF₄ plasma treatment is conducted for 30 minutes with a CF₄ gas flow volume of 900 SCCM, a power of 1.0 W/cm², and a pressure of 1 torr. Atmospheric-pressure plasma treatment may also be performed under conditions of an electrode-substrate distance of 1 mm, CF₄ gas flow volume of 100 ccm, helium gas flow volume of 10 liter/min, and transporting speed of 5 mm/s. The polyimide surface can be modified to a Teflon-treated liquid-repellent surface 305 while maintaining the hydrophilic ITO surface 303.

[0208] When the contamination on the substrate surface is of a mild degree, similar effectiveness can be obtained, without conducting the oxygen plasma treatment, by performing the CF₄ plasma treatment for 30 to 60 minutes under conditions of a CF₄ gas flow volume of 900 SCCM, power of 1.0 W/cm², and pressure of 1 torr.

[0209] In the process diagrammed in Fig. 23D, a hole injection layer 306 is formed by spin coating. By adjusting the surface tension of the hole injection layer material liquid, the hole injection layer material can be patterned exclusively inside the ITO pixels. The spin-coating solution used was a water dispersion of polyethylene dioxythiophene and polystyrene sulfonic acid diluted with ethoxy ethanol and methanol (totaling 75 percent) and adjusted to a surface tension of 30 dyne/cm. For the hole injection layer material liquid, the plasma-treated ITO surfaces exhibit an angle of contact of 10 degrees or less, and are therefore evenly coated. At the plasma-treated polyimide surface, moreover, an angle of contact of 60 degrees or greater is exhibited, wherefore the banks are not coated, and no cross-talk is induced. A hole injection layer material ink may also be formed as a patterned film inside the ITO pixels by an ink jet process. The method of the ink jet process can yield significant savings in material.

[0210] In Fig. 23E, light emitting layers are formed in three colors, R, G, and B, by discharging a red light emitting layer material ink 307, a green light emitting layer material ink 308, and a blue light emitting layer material ink 309 into respectively prescribed pixels from an ink jet head 310. The ink used for the green light emitting layer material was made by diluting a PPV precursor liquid with a mixture liquid of DMF, glycerin, and diethylene glycol. The ink used for the red light emitting layer material was made by adding red pigment rhodamine 101 to the green ink made with PPV, in a ratio of 1.5 wt% relative to the PPV. The ink used for the blue light emitting layer material was an ink made by dissolving a polydioctyl sulfluorine in xylene. The angles off contact of the light emitting material layer inks 307, 308, and 309 on the plasma-treated polyimide surfaces are 60 degrees or greater, wherefore superfine patterning is possible with no color mixing. When forming monochrome organic EL elements, the light emitting layer can be formed by spin coating.

[0211] By employing the plasma treatments described above, a substrate may also be used whereon banks are formed in two layers, employing a glass layer for the lower layer so that the angle of contact with the hole injection layer material liquid or light emitting layer ink is within a range of 20 to 30 degrees. It is possible to avoid the danger of shorting at the bank skirts.

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(10) Tenth Embodiment

[0212] A thin film formation method and a manufacturing method for color filters comprising colored thin films relating to a tenth embodiment of the present invention are now described, making reference to the drawings.

[0213] Fig. 24A - 24D are process cross-sections representing a color filter manufacturing method.

[0214] In the process diagrammed in Fig. 24A, a resin BM (black matrix) 312 is formed by photolithography on a glass substrate 311. The pattern may be a striped pattern or a pattern wherein circular shapes are removed.

[0215] In the process diagrammed in Fig. 24B, an oxygen plasma treatment is performed for 1 minute with an oxygen gas flow volume of 500 SCCM, power of 1.0 W/cm², and pressure of 1 torr as conditions. Atmospheric-pressure plasma treatment can also be performed with a power of 300 W, electrode-substrate distance of 1 mm, oxygen gas flow volume of 80 ccm, helium gas flow volume of 100 liters/min, and transporting speed of 10 mm/s. In the oxygen plasma treatment a hydrophilic glass surface 13 and a resin BM layer 314 that is activated (made hydrophilic) are formed. The oxygen plasma treatment exhibits effectiveness in ashing resin residue on the glass.

[0216] Following thereupon, in the process diagrammed in Fig. 23C, CF₄ plasma treatment is conducted for 30 minutes with a CF₄ gas flow volume of 900 SCCM, a power of 1.0 W/cm², and a pressure of 1 torr. Atmospheric-pressure plasma treatment may also be performed under conditions of an electrode-substrate distance of 1 mm, CF₄ gas flow volume of 100 ccm, helium gas flow volume of 10 liter/min, and transporting speed of 5 mm/s. The resin BM surface can be modified to a Teflon-treated ink-repellent surface 315 while maintaining the hydrophilic glass surface 313.

[0217] When the contamination on the substrate surface is of a mild degree, similar effectiveness can be obtained, without conducting the oxygen plasma treatment, by performing the CF₄ plasma treatment for 30 to 60 minutes under conditions of a CF₄ gas flow volume of 900 SCCM, power of 1.0 W/cm², and pressure of 1 torr.

[0218] In the process diagrammed in Fig. 24D, a filter layer is formed in three colors, R, G, and B, by discharging a red light transmitting pigment ink 316, a green light transmitting pigment ink 317, and a blue light transmitting pigment ink 318 in respectively prescribed pixels from an ink jet head 319. The angles of contact of the pigment inks 317, 318, and 319 on the plasma-treated resin BM surface are 60 degrees or greater, wherefore superfine patterning is possible with no color mixing.

[0219] By employing the plasma treatments described above, a substrate may also be used whereon banks are formed in two layers, employing a material for the lower layer wherewith the angle of contact with the pigment ink is within a range of 20 to 50 degrees. It is possible to avoid the danger of color loss and film thickness irregularities.

(11) 11th Embodiment

[0220] A surface modification method and thin film formation method relating to an 11th embodiment of the present invention are now described, making reference to the drawings.

[0221] Fig. 25A - 25D diagram the benefits of forming banks in two layers, namely of an inorganic substance and of an organic substance.

[0222] In the process diagrammed in Fig. 25A, laminated banks comprising a glass lower layer 321 and a polyimide upper layer 322 are formed by photolithography on an ITO substrate 20.

[0223] In the process diagrammed in Fig. 25B, the oxygen plasma and fluorine plasma treatments indicated in the eighth to tenth embodiments are conducted successively. The ITO substrate layer and the lower bank layer glass surface are made hydrophilic, while the upper bank layer polyimide is made liquid-repellent.

[0224] In the process diagrammed in Fig. 25C, liquid thin film materials having different characteristics are coated in adjacent depressions by discharging a thin film material ink A 327 and a thin film material ink B 328 from an ink jet head 326. After the plasma treatment, the angles of contact indicated for the thin film material ink are 20 degrees or less at the ITO surface 323, 30 to 40 degrees in the lower bank layer glass surface 324, and 90 degrees in the upper bank layer polyimide surface 325.

[0225] After baking, as diagrammed in Fig. 25D, the thin films A 329 and B 330 are obtained. The plasma-treated polyimide surface 325 exhibits strong ink repellency, wherefore, a flat film is sometimes not formed about periphery of the bank skirts that are formed of polyimide. However, the ITO surface 323 and the glass surface 324 both exhibit ink affinity, wherefore film formation also occurs about the periphery of the lower bank skirts formed of glass and a flat film is formed on the ITO surface. In the case of an element structured with an organic thin film sandwiched between ITO and an electrode, as in an organic EL element, it is possible to prevent shorts from occurring because no film is formed on the ITO. In the manufacture of color filters, moreover, this is very effective in preventing the color irregularities caused by film thickness irregularities.

[0226] As based on the eighth to 11th embodiments, as described in the foregoing, after subjecting a substrate having banks formed of an organic substance on the same substrate to an oxygen gas plasma treatment, that substrate is immediately subjected to a fluorine-based gas plasma treatment, thereby imparting semi-permanent liquid repellency to the banks while maintaining the liquid affinity of the substrate surface.

[0227] By using the methods described in the foregoing, furthermore, patterns wherein the surface energy is controlled can be formed by a simple method on the same substrate, whereupon it becomes possible to form finely patterned films with liquid thin film materials, not only using conventional coating methods such as spin coating, but also using a coating method based on an ink jet process. That being so, it becomes possible to manufacture color filters and full-color organic EL devices without color mixing, color irregularity, or cross-talk, simply and at low cost.

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Claims

FIG.23A

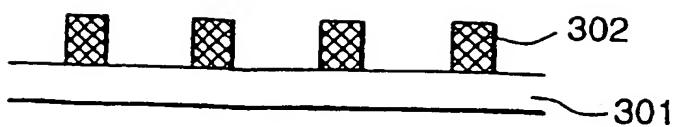


FIG.23B

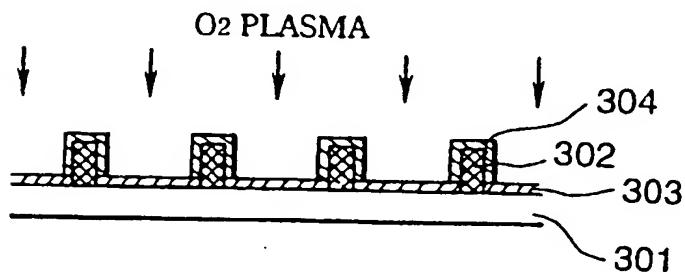


FIG.23C

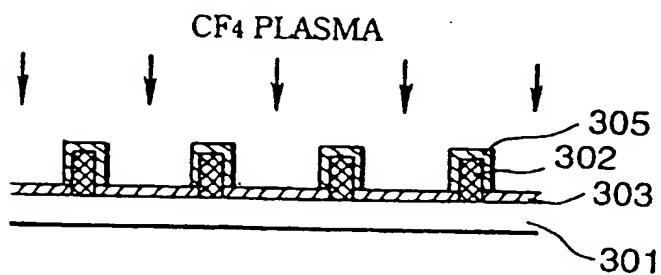


FIG.23D

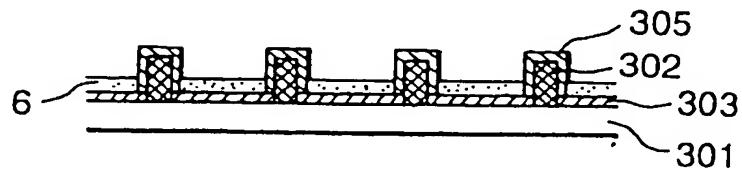


FIG.23E

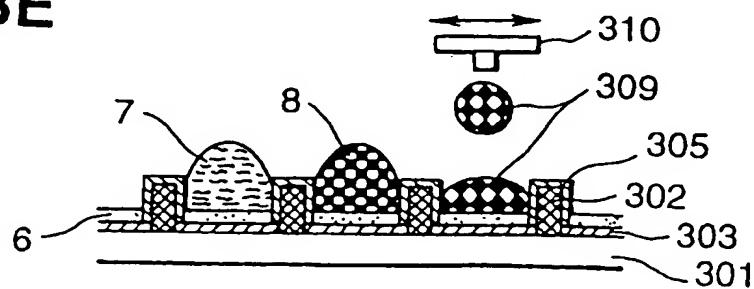


FIG.24A

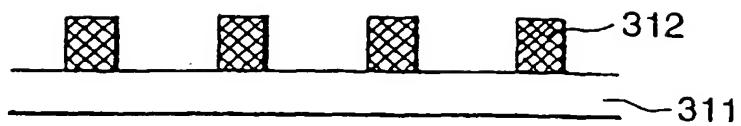


FIG.24B

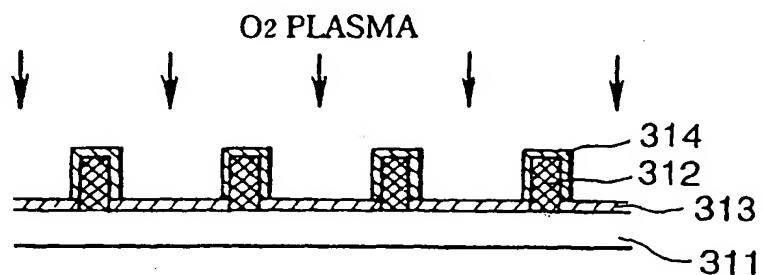


FIG.24C

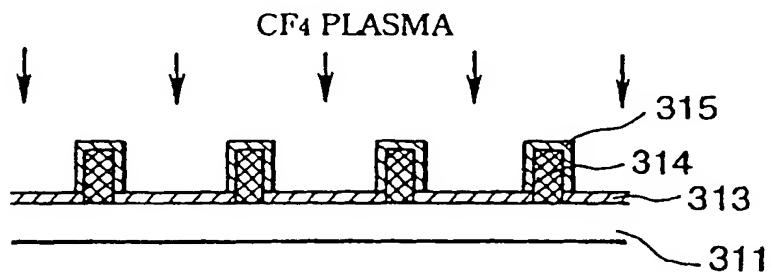


FIG.24D

